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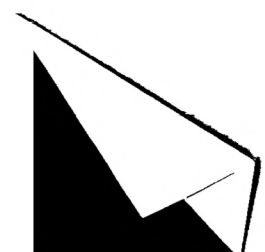
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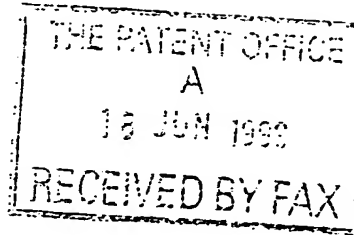
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18JUN99 E455615-1 D02776
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1. Your reference

IPD/P1242

2. Patent application number

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18 JUN 1999

3. Full name, address and postcode of the or of each applicant (underline all surnames)

The Secretary of State for Defence
Defence Evaluation & Research Agency
Ively Road
Farnborough, Hampshire, GU14 0LX

Patents ADP number (if you know it)

54510004

If the applicant is a corporate body, give the country/state of its incorporation

GB

4. Title of the invention

EPOXIDE COATINGS

5. Name of your agent (if you have one)

BOWDERY A O

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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Formalities Section
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MOD Abbey Wood # 19
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BS34 8JH

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Country

Priority application number
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Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number or earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

Yes

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
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Patents Form 1/77

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Description 9.

Claim(s) 2

Abstract 1

Drawing(s) 5

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Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination 1
and search (Patents Form 9/77)Request for substantive examination
(Patents Form 10/77)Any other documents
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11.

I / We request the grant of a patent on the basis of this application.

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S R Skelton

Date 18/06/1999

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Patents Form 1/77

Epoxide Coatings

This invention relates to the coating of surfaces with an epoxide layer. More particularly the present invention relates to the production of an epoxide layer on a surface, as well as to coated articles obtained thereby.

Deposition of an epoxide layer on a wide variety of surfaces is a widely used technique. For example, it may be desirable to provide such a layer on solid surfaces, such as metal, glass, ceramics, paper, polymers and the like in order to improve adherent properties, or to facilitate chemical grafting or laminating of surfaces. Such a layer may also be deposited on a fabric, fibre or garment.

Plasma deposition techniques have been quite widely used for the deposition of polymeric coatings onto a range of surfaces. This technique is recognised as being a clean, dry technique that generates little waste compared to conventional wet chemical methods. Using this method, plasmas are generated from small organic compounds which are subjected to an ionising electric field under low pressure conditions. When this is done in the presence of a substrate, the ions, radicals and excited molecules of the compound in the plasma polymerise in the gas phase and react with a growing polymer film on the substrate. Conventional polymer synthesis tends to produce structures containing repeat units which bear a strong resemblance to the monomer species, whereas a polymer network generated using a plasma can be extremely complex.

The success or otherwise of plasma polymerisation depends upon a number of factors, including the nature of the organic compound. Reactive oxygen containing compounds such as maleic anhydride, has previously been subjected to plasma polymerisation (Chem. Mater. Vol. 8, 1, 1996).

Plasma techniques have been widely used for the deposition of oil or water repellent finishes. For example, US Patent No 5,328,576 describes the treatment of fabric or paper surfaces to impart water- and oil-repellent properties by subjecting the surface to a pre-treatment with an oxygen plasma, followed by plasma polymerisation of methane. However, plasma polymerisation of epoxide compositions has previously proved difficult to achieve.

The applicants have found an improved method of producing surface coatings containing high levels of epoxide groups. Preferably the coatings are suitable for use as adhesive coatings.

According to the present invention there is provided a method of coating a surface with an epoxide layer, which method comprises exposing said surface to a plasma comprising an epoxide.

Preferably, the epoxide is an unsaturated epoxide, although the present inventors have found that saturated epoxides can also be deposited by this method.

The epoxide may be substituted. The substituent is preferably selected from the group comprising allylic, halogen, aryl, alkyl and aromatic moieties.

In a most preferred embodiment, the epoxide used is glycidyl acrylate.

The surface coated in accordance with the invention may be of any solid substrate, such as fabric, metal, glass, ceramics, paper or polymers. In particular, the surface comprises a fabric substrate such as a cellulosic fabric, to which an epoxide layer is to be applied.

Preferably, the epoxide layer is suitable for use as an adhesive layer.

The precise conditions under which the plasma polymerization takes place in an effective manner will vary depending upon factors such as the nature of the polymer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of compounds of formula (I) at pressures of from 0.01 to 10 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

The applied fields are suitably of average power of up to 50W. Suitable conditions include pulsed or continuous fields, preferably pulsed fields. The pulses are applied in a sequence which yields very low average powers, for example in a sequence in which the power is on for 20(s and off for 1000(s.

The fields are suitably applied from 30 seconds to 20 minutes, preferably from 2 to 15 minutes, depending upon the nature of the compound of formula (I) and the substrate etc.

Plasma polymerisation of compounds of formula (I), particularly at low average powers has been found to result in the deposition of substantially intact monomers, in particular it has been found that the 3-membered oxirane rings have been found retain a high level of functional integrity.

The greater level of structural retention in the case of pulsed plasma polymerisation can be attributed to free radical polymerisation occurring during the duty cycle off-time and less fragmentation during the on-time (M. Lewin et al., 'Handbook of Fibre Science and Technology' Marcel and Dekker Inc., New York, (1984) Vol 2, Part B Chapter 2).

The present inventors have also found that when a substrate bearing an adhesive layer in accordance with the invention is contacted with a second surface bearing a nucleophilic layer in order to bond the substrates to one another.

Accordingly, the present invention provides a method of bonding substrates, the method comprising applying an adhesive layer to a substrate by plasma deposition, contacting the adhesive layer with a nucleophilic layer, and heating the two substrates to effect bonding.

The invention will now be particularly described by way of example with reference to the accompanying drawing, of which

Figure 1 which shows a diagram of the apparatus used to effect plasma deposition;

Figure 2 shows the peaks obtained with pulsed plasma polymerisation;

Figure 3 shows the infra-red spectra of the monomer and the plasma polymers;

Figure 4 shows peaks of the labelled polymers, and

Figure 5 shows the infra-red spectrum of the pulsed plasma polymer.

Example 1

Plasma Polymerisation of Glycidyl acrylate.

Glycidyl acrylate was placed into a monomer tube (1) (Fig. 1) and further purified using freeze-thaw cycles. A series of plasma polymerisation experiments were carried out in an inductively coupled cylindrical plasma

reactor vessel (2) of 5cm diameter, 470cm³ volume, base pressure of 7x10⁻³ mbar, and with a leak rate of better than 2x10⁻³ cm³min⁻¹. The reactor vessel (2) was connected by way of a "viton" O-ring (3), a gas inlet (4) and a needle valve (5) to the monomer tube (1).

A thermocouple pressure gauge (6) was connected by way of a Young's tap (7) to the reactor vessel (2). A further Young's tap (8) connected with an air supply and a third (9) lead to an E2M2 two stage Edwards rotary pump (not shown) by way of a liquid nitrogen cold trap (10). All connections were grease free.

An L-C matching unit (11) and a power meter (12) was used to couple the output of a 13.56 Mhz R.F. generator (13), which was connected to a power supply (14), to copper coils (15) surrounding the reactor vessel (2). This arrangement ensured that the standing wave ratio (SWR) of the transmitted power to partially ionised gas in the reactor vessel (2) could be minimised. For pulsed plasma deposition, a pulsed signal generator (16) was used to trigger the R.F power supply, and a cathode ray oscilloscope (17) was used to monitor the pulse width and amplitude. The average power <P> delivered to the system during pulsing is given by the following formula:

$$\langle P \rangle = P_{cw} \{ T_{on} / (T_{on} + T_{off}) \}$$

where $T_{on} / (T_{on} + T_{off})$ is defined as the duty cycle and P_{cw} is the average continuous wave power.

In order to carry out polymerization/deposition reactions the reactor vessel (2) was cleaned by soaking overnight in a chlorox bleach bath, then scrubbing with detergent and finally rinsing with isopropyl alcohol followed by oven drying. The reactor vessel (2) was then incorporated into the assembly as shown in Figure 1 and further cleaned with a 50W air plasma for 30 minutes. Next the reactor (2) vessel was vented to air and the substrate to be coated

(19), in this case a glass slide, was placed in the centre of the chamber defined by the reactor vessel (2) on a glass plate (18). The chamber was then evacuated back down to base pressure (7.2×10^{-3} mbar).

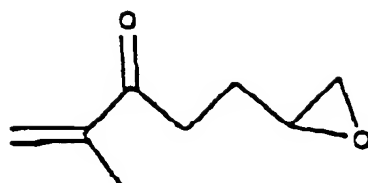
Glycidyl methacrylate vapour was then introduced into the reaction chamber at a constant pressure of ~ 0.2 mbar and allowed to purge the plasma reactor, followed by ignition of the glow discharge. Typically 2-15 minutes deposition time was found to be sufficient to give complete coverage of the substrate. After this, the R.F generator was switched off and the perfluoroalkene vapour allowed to continue to pass over the substrate for a further 5 minutes before evacuating the reactor back down to base pressure, and finally venting up to atmospheric pressure.

The deposited plasma polymer coatings were characterised immediately after deposition by X-ray photoelectron spectroscopy (XPS). Complete plasma polymer coverage was confirmed by the absence of any Si (2p) XPS signals showing through from the underlying glass substrate.

A control experiment, where the fluoroalkene vapour was allowed to pass over the substrate for 15 minutes and then pumped down to base pressure was found to show the presence of a large Si (2p) XPS signal from the substrate. Hence the coatings obtained during plasma polymerisation are not just due to adsorption of the fluoroalkene monomer onto the substrate.

The experiments were carried out with average powers in the range of from 0.3 to 50W.

As can be seen in Figure 2, the C 1s peaks of the CW (2) and the pulsed (3) plasma polymers are displayed together with the theoretical one, and, as expected, form the conventional polymerisation of the monomer (structure I)



(i)

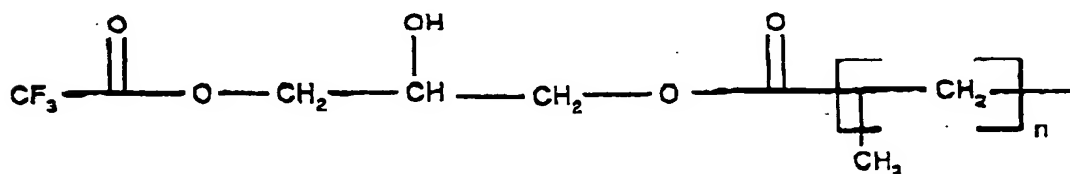
The peak fittings derived from Briggs (Beamson, G; Briggs, D; *High resolution XPS of Organic Polymers, The Scienta ESCA Database*, John Wiley & Sons: New York, 1992; pp 130-131) are also shown, no peak fitting was possible for the CW plasma polymer on the base of the monomer structure. The peak shape however suggests that the CW plasma polymer is rich in hydrocarbon content (285 eV component), and little of the original structure was preserved in the polymerisation process. The shoulder at higher binding energies indicates the presence of small amounts of C=O and epoxy rings.

The pulsed plasma polymer instead has a peak that reflects the expected one. The peak fitting showed that 19% of the epoxy group was present on the surface, which means that more than 95% of the original functionality was retained.

With reference to Figure 3 the IR spectra of the monomer (i), the CW plasma polymer are shown. The pulsed polymer spectrum is better resolved than the CW plasma polymer, the latter showing broad peaks. The CW and the pulsed polymer spectra show no features due to C=C stretching as shown by the monomer spectrum, which means that the unsaturation is destroyed in the polymerisation process. The C=O stretching is present in all the three spectra, the monomer one occurring at a higher wavenumber due to the conjugation with the double bond. The features due to epoxy groups (Lin-Vien, D; Colthup, N, B; Fately W,G; Graseeli J,G; *The Handbook of infra-red and Raman Characteristic Frequencies of Organic Molecules*, Academic

Press: New York, 1991:p 67) are put into evidence. They are present in both the CW and the pulsed plasma spectra but are better resolved and more intense in the second. This result is in accordance with the XPS, which showed a high retention of epoxy group in the pulsed plasma polymer and indicated the presence of the ring also in the CW plasma polymer.

Referring to Figure 4 which shows the C1s peaks of the CW (i) and the pulsed (ii) plasma polymers labelled with CF_3COOH , no peak fitting was possible due to the complexity of the structure after labelling. The proposed structure after labelling is shown below (Structure II) and is derived from nucleophilic attack of the acidic oxygen on the less hindered epoxy carbon (Structure II)



(II)

However, the well resolved CF_3 peak was fitted in order to quantify it. The area of the CF_3 peak is reported in relation to the total area of the carbon peak. The values for the two polymers are shown in Table 1.

TABLE 1

| | Area CF_3 % |
|--------|------------------------|
| | Area C - CF_3 |
| CW | $1.5 \pm 0.5 \%$ |
| Pulsed | $6.8 \pm 0.5 \%$ |

As expected the amount of CF_3 is smaller for the CW plasma polymer than for the pulsed plasma polymer, as a consequence of the lower concentration of the epoxy groups. The observation of a small CF_3 peak and a small amount of fluorine on the surface however confirms the presence of epoxy rings also in the CW plasma polymer.

Figure 5 shows the infra-red spectrum of the pulsed plasma polymer labelled with CF_3COOH and no feature of the original polymer can be recognised, whereas new features are present. This indicates that the reaction with the acid involved a whole new polymer layer. The broad absorption due to O-H stretching and the C=O stretching occurring at a lower wavenumber (1682 cm^{-1}) than expected for an ester carbonyl suggest that a hydrogen bond is formed and this can be due to either an intramolecular interaction between the O-H and the O=C that gives rise to a seven membered ring , or an intermolecular interaction between adjacent tails in the polymer backbone.

Claims

1. A method of coating a surface with an epoxide layer, which method comprises exposing said surface to a plasma comprising an epoxide.
2. A method according to claim 1 wherein the said epoxide is saturated.
3. A method according to any one of the preceding claims wherein the surface is a surface of a fabric, metal, glass, ceramics, paper or polymer substrate.
4. A method according to any one of the preceding claims wherein the gas pressure of the organic compound is from 0.01 to 10 mbar.
5. A method according to any one of the preceding claims wherein a glow discharge is ignited by applying a high frequency voltage of 13.56mhz.
6. A method according to claim 5 wherein the voltage is applied as a continuous field.
7. A method according to claim 7 wherein the voltage is applied as a pulsed field.
8. A method according to claim 7 wherein pulses are applied in a sequence which yields low average power.
9. A method according to claim 8 wherein the sequence is such that the power is on for 20(s and off for 10000(s.
10. A methods according to any one of the preceding claims wherein the plasma polymerisation takes place for from 2 to 15 minutes.

11. A method according to any preceding claim in which the epoxide layer is usable as an adhesive.

12. A method of bonding substrates, the method comprising applying an adhesive layer to a substrate by plasma deposition, contacting the adhesive layer with a nucleophilic layer, and heating the two substrates to effect bonding.

Abstract

A method of coating a surface with an epoxide layer, in particular an adhesive epoxide layer, which method comprises exposing said surface to a plasma comprising an epoxide compound. Any epoxide coating may be applied in this way.

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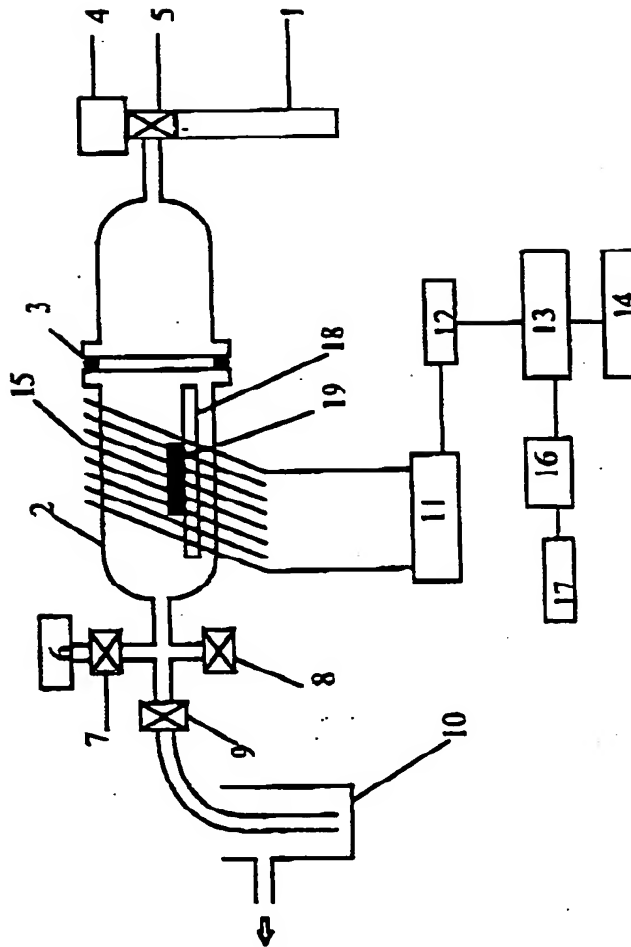
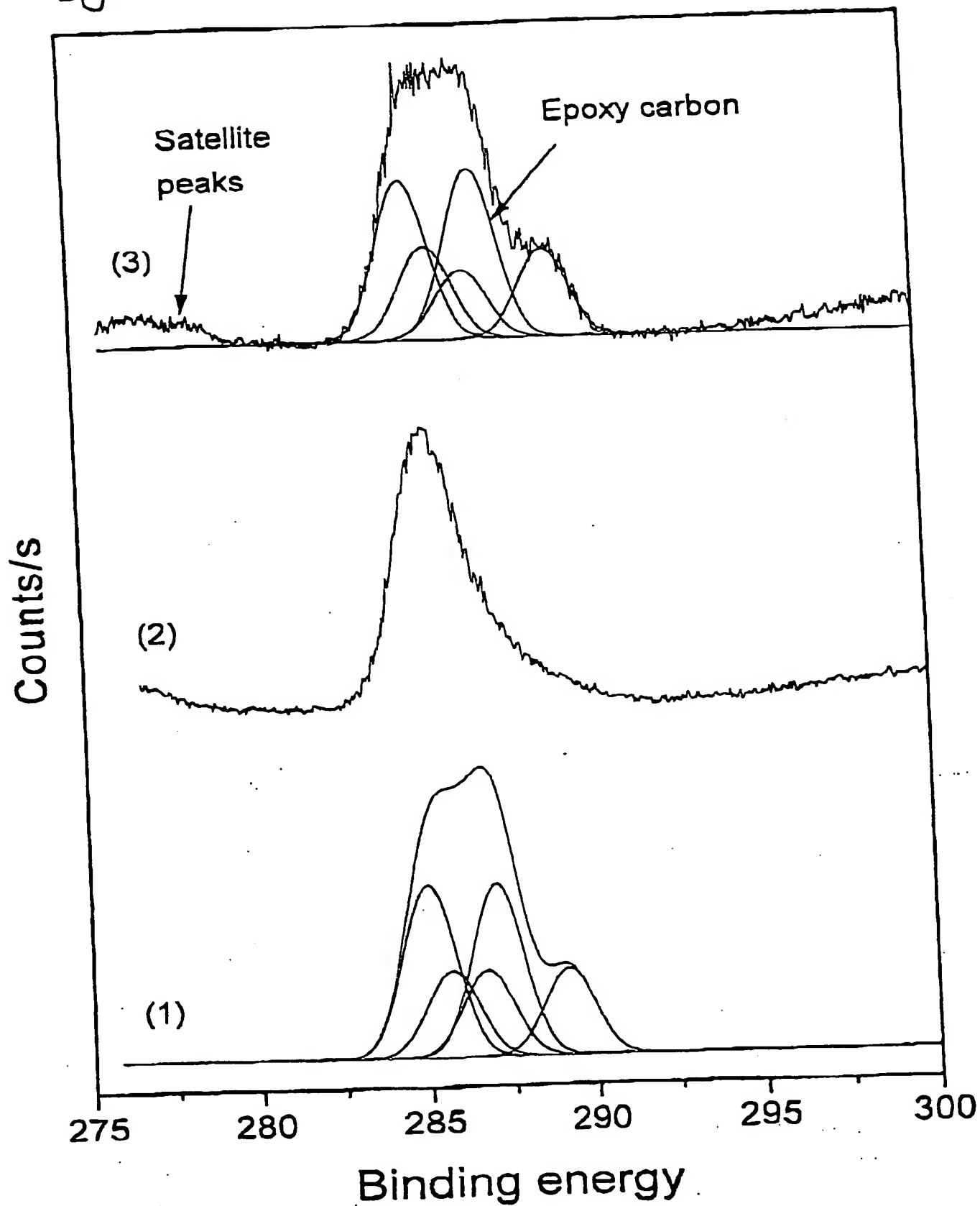
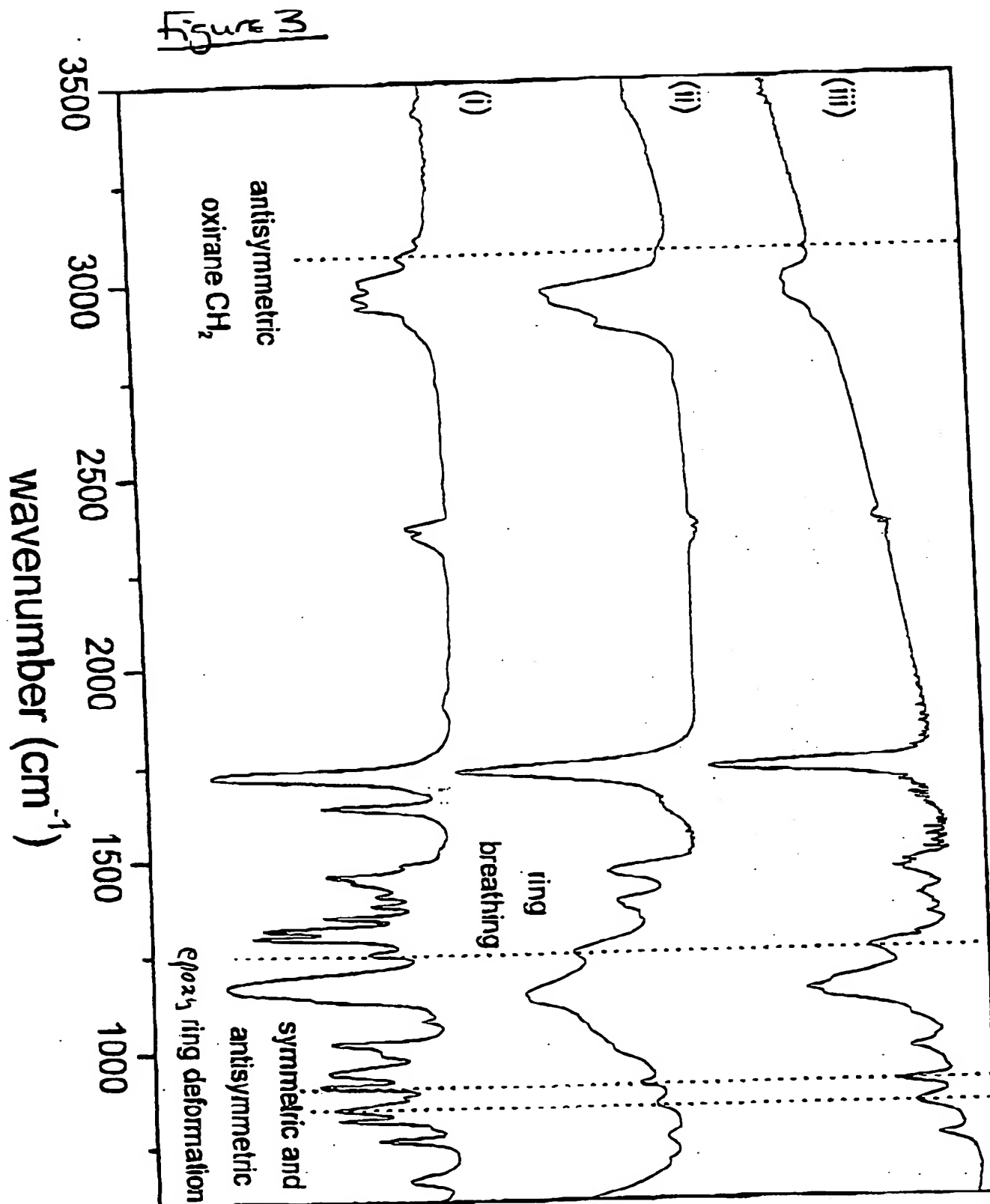


Figure 1.

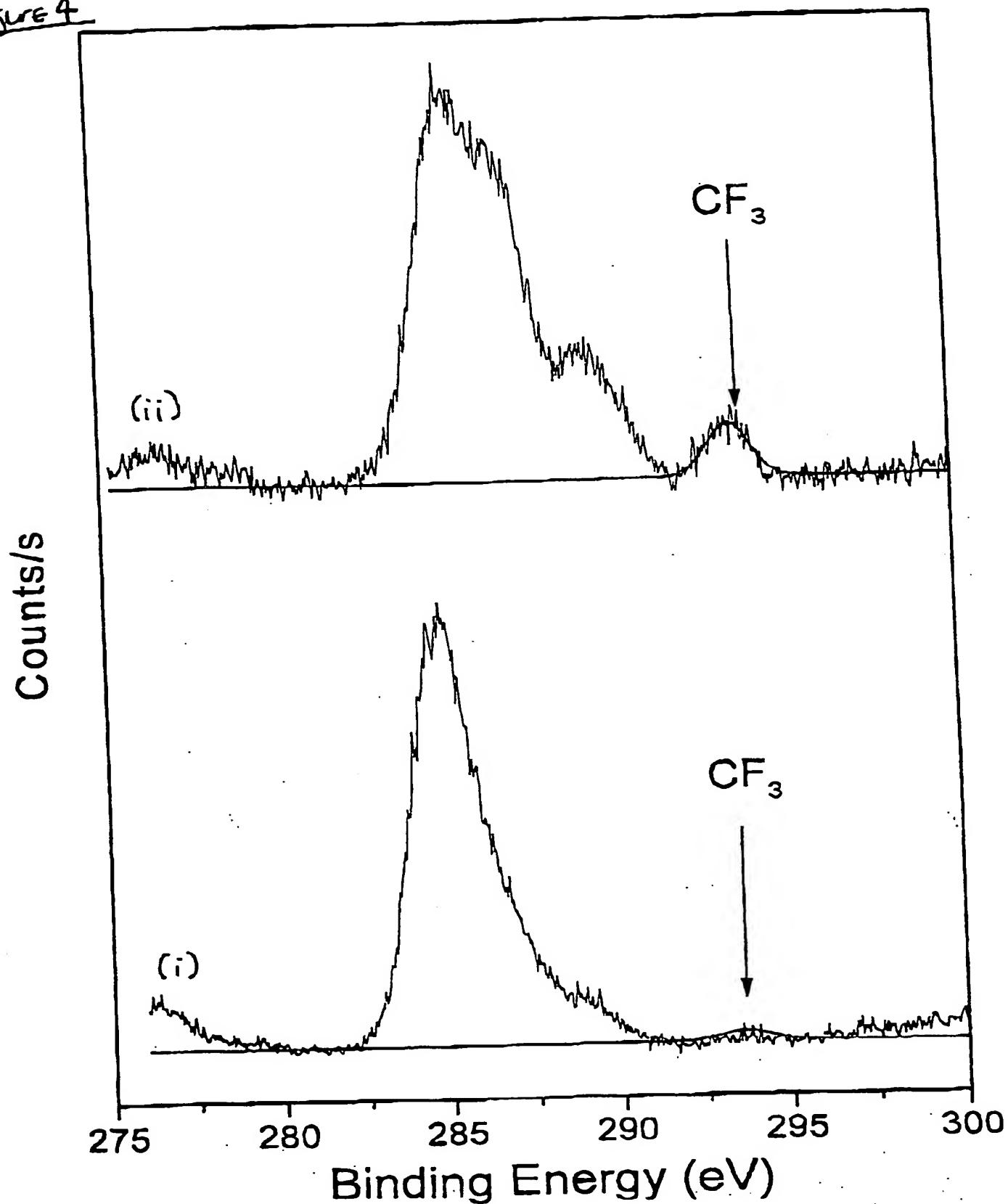
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Figure 2

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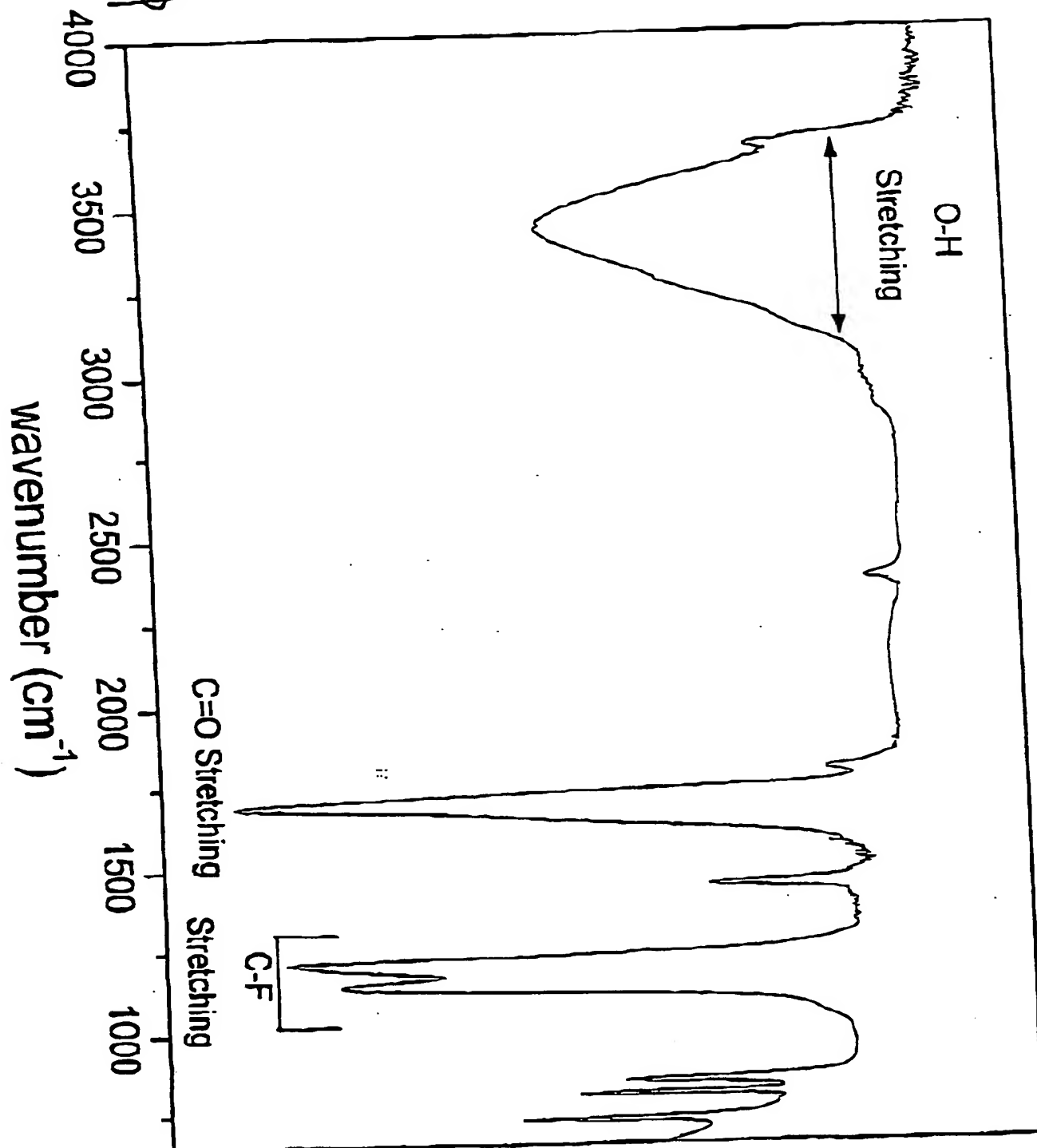


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Figure 4

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Figure 5



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